15

30

Annex Chapter II-Report

# Replace AP20 Rec'd PCT/PTO 09 JUN 2006

According to the present invention, this object is achieved by a method as claimed in claim 1, wherein the monomers (A), (B), and (C) preferably come to more than 90 wt.% of the incorporated monomers, especially more than 95 wt.%, and as claimed in claims 4 and 12.

Preferred embodiments of the subject invention are set out in the subordinate claims or will be apparent from the ensuing description.

The use of the redeposition inhibitors described in the method of the invention results in very little backstaining, accompanied by an excellent stonewashed look.

Use of the redeposition inhibitors described in the method of the invention results in very little backstaining, accompanied by an excellent stonewashed look.

According to the present invention, the object is achieved by utilizing polymers known as soil release polymers, which are preferably amphiphilic polyether monomer sequences, more preferably nonionic polyester-containing ones.

- The polyether monomer sequences are produced from polyetherols. The term 'polyetherols' as used herein refers to compounds with one or two hydroxy groups having at least 6 oxygen atoms, preferably at least 10 oxygen atoms, more preferably more than 16 oxygen atoms.
- By the term 'diols' as used herein is meant compounds having two hydroxy groups and not more than one ether group, preferably none.

According to an embodiment of the present invention, it is preferable to use liquid polyesters, which are free-flowing at room temperature and hence especially appropriate for incorporation into liquid stonewashing formulations. Said polyesters can be produced by reaction, preferably polycondensation, of

10

15

20

25

30

35

### Replacement Page

- (A) 20 to 50 mole% of one or more dicarboxylic acid compound(s),
- (B) more than 0 to 30 mole% of one or more diol compound(s) having from 2 to 6 carbon atoms,
- (C) 10.1 to 50 mole% of one or more water-dilutable polyetherol(s), which can be produced by the addition of one or more C<sub>2</sub>- to C<sub>4</sub>-alkylene oxide(s) to a C<sub>1</sub> to C<sub>18</sub> alcohol, especially a C<sub>1</sub> to C<sub>6</sub> alcohol, with one hydroxy group, wherein the alkylene oxide/alcohol mole ratio is in the range from 4 to 100: 1, and
- (D) 10.1 to 29.9 mole % of one or more polyol compound(s) having at least 3 OH groups.

The compounds described hereinabove and their preferred variants have been disclosed in WO 02/18474-A1 which, with regard to the definition of said compounds, is completely incorporated herein by reference.

The statements related to mole % made hereinabove are to be understood as final and independent of one another and refer to the total of the components (A) to (D). The polyester was made utilizing essentially no additional component, i.e. <5 mole% of additional component(s), preferably <1 mole%. As used herein, the term 'room temperature' means a temperature from 15 °C to 25 °C, especially 20°C.

According to the main claim of the present invention, the term 'compounds' employed herein is defined as organic compounds, which usually do not contain any other atoms besides carbon, hydrogen, and oxygen after the reaction, i.e. incorporation into the polymer. For example, after incorporation into the polyester, the dicarboxylic acid compounds may have carboxyl groups besides carbonyl groups or hydroxy groups, but do not have sulfonyl- or halogen groups for instance.

The dicarboxylic acid compound (A) includes aliphatic and/or aromatic dicarboxylic acids and their derivatives, e.g. their monoesters, diesters, anhydrides, or mixtures. The dicarboxylic acid compounds preferably have 3 to 40 carbon atoms, related to the dicarboxylic acid or the dicarboxylic acid group. According to the present invention, the aromatic dicarboxylic acid compounds may especially be terephthalic acid, isophthalic acid, phthalic acid, their mono- and dialkyl esters having C<sub>1</sub>- to C<sub>5</sub>- alcohols, e.g. dimethyl terephthalate, and mixtures of said

- d) acyl- and aroyl groups having from 4 to 40 carbon atoms,
- e) hydroxyacyl- and hydroxyaroyl groups having from 2 to 25 carbon atoms,
- f) poly(oxyalkylene)monoalkyl phenol ether, wherein the alkyl group has from 6 to 18 carbon atoms and the polyoxyalkylene group is comprised of 0 to 80 oxyalkylene units

and mixtures thereof.

Nonionic PET-(polyethylene terephthalate)-POET (polyoxyethylene terephthalate)-polyesters are particularly preferred. Said polyesters can be produced by polycondensation of terephthalic acid or terephthalates with monoethylene glycol and polyethylene glycol. It is preferable to use polyethylene glycols having molecular weights from 2,000 to 10,000 g/mole. It is also preferable that the resultant PET-POET copolymers be solid at room temperature and have mean molecular weights from 5,000 to 40,000 g/mole.

In addition, polyester-polyether copolymers, which are liquid at room temperature, are preferably employed. Said copolymers may be composed according to the formula

 $X-(OCH_2-CH_2)_n-[-(OOC-R^1-COO-R^2)_u-]-OOC-R^1-COO-(CH_2-CH_2O)_n-X$ , wherein each  $\mathbf{R}^1$  residue is a 1,4-phenylene residue, optionally substituted by mono- or di-C<sub>1</sub>-C<sub>3</sub>-alkyl; the  $\mathbf{R}^2$  residues are principally ethylene residues, 1,2-propylene residues, or mixtures thereof; each  $\mathbf{X}$  represents independently of one another hydrogen, a C<sub>1</sub> to C<sub>12</sub> hydrocarbon residue, especially ethyl or methyl; each  $\mathbf{n}$  is independently of one another from 7 to 115, and  $\mathbf{u}$  is from 3 to 10.

5

10

15

20

25

## Replacement Page

The synthesis of the polymers employed according to the present invention may be carried out as a direct reaction of all the monomer units in a single step yielding random polymers. According to another method, the synthesis may also be carried out in several steps, e.g. including precondensation of various building monomers.

Normally, the temperature is in the range from about 80 °C to 350 °C and the pressure range is from normal to <1 mbar. It is preferable to carry out the condensation at

10

5

15

20

25

30

35

D03008 HC CHIL spec

#### **Patent Claims**

5

10

20

1. A method of preventing or minimizing dye redeposition onto textile fabrics during stonewashing and/or biostoning of indigo-dyed cotton fabrics by contacting the dyed fabric comprising cotton fibers with a dye redeposition inhibitor during the dye removal process,

**characterized in that** the dye redeposition inhibitor is a polyester, which is produceable by reacting at least the following monomers during an esterification reaction:

- (A) one or more dicarboxylic acid compound(s), wherein terephthalic acid makes up more than 90 mole% of the dicarboxylic acid compounds employed,
- (B) one or more diol compound(s) having from 2 to 6 carbon atoms, wherein the ethylene glycol makes up more than 90 mole% of the diol compounds employed, and
- 15 (C) polyetherols with one or two hydroxy groups having at least 6 oxygen atoms, wherein polyethylene glycol having a molecular weight from 2,000 to 8,000 g/mole makes up more than 90 wt.% of the polyetherols employed, and the monomers (A), (B), and (C) result in more than 80 wt.% of the incorporated monomers.

2. The method according to claim 1,

characterized in that the monomers (A), (B), and (C) come to more than 90 wt.% of the incorporated monomers, particularly more than 95 wt.%

- A method according to any one of the preceding claims,
   characterized in that the polyesters is furthermore produceable by using
  - (D) one or more polyol compound(s) with at least 3 OH groups having from 3 to 12 carbon atoms, especially glycerol.
- 4. A method of preventing or minimizing dye redeposition onto textile fabrics by contacting the dyed fabric comprising cotton fibers with a dye redeposition inhibitor during the dye removal process,

**characterized in that** the dye redeposition inhibitor is a polyester, which is produceable by reacting at least the following monomers during an esterification reaction:

35 (A) 20 to 50 mole% of one or more dicarboxylic acid compound(s),

10

30

### Replacement Page

- (B) more than 0 to 30 mole% of one or more diol compound(s) having from 2 to 6 carbon atoms,
- (C) 10.1 to 50 mole% of one or more water-dilutable polyetherol(s), which can be produced by the addition of one or more C<sub>2</sub>- to C<sub>4</sub>-alkylene oxide(s) to a C<sub>1</sub> to C<sub>18</sub> alcohol, especially a C<sub>1</sub> to C<sub>6</sub> alcohol, with one hydroxy group, wherein the alkylene oxide/alcohol mole ratio is in the range from 4 to 100: 1, and
- (D) 10.1 to 29.9 mole % of one or more polyol compound(s) having at least 3 OH groups.
- 5. The method according to claim 4, characterized in that 1 to 10 mole% of the diol compound (B) is incorporated.
- 6. A method according to any one of claims 4 or 5,

  characterized in that the average molecular weight of the polyester is less 5,000 g/mole, preferably from 2,000 to 5,000 g/mole.
- 7. A method according to any one of the preceding claims, characterized in that the dicarboxylic acid compounds (A) comprise terephthalic acid, isophthalic acid, and phthalic acid and their derivatives, especially terephthalic acid and its derivatives, preferably in a quantity of greater 90 mole% of terephthalic acid and its derivatives, based on the incorporated dicarboxylic acid compounds.
  - 8. A method according to any one of the preceding claims,
- 25 **characterized in that** independently of one another
  - (a) no tricarboxylic acid compounds and
  - (b) less than 10 wt.% of isophthalic acid or its derivatives and especially no isophthalic acid or its derivatives are employed.
  - 9. A method according to any one of the preceding claims, characterized in that the diol compound (B) is ethylene glycol and/or propylene glycol.

10. A method according to any one of the preceding claims, characterized in that the polyester is anionically modified by incorporation of anionic monomers and/or is capped with terminal groups.

5

11. A method according to any one of the preceding claims, characterized in that the polyetherols (C) are alkylene oxide addition products of ethylene oxide, propylene oxide, butylene oxide or their mixtures to aliphatic  $C_1$  to  $C_{18}$  alcohols, preferably  $C_1$  to  $C_6$  alcohols, and/or water to water or methanol.

10

- 12. A method of preventing or minimizing dye redeposition onto textile fabrics during stonewashing and/or biostoning of indigo-dyed cotton fabrics by contacting the dyed fabric comprising cotton fibers with a dye redeposition inhibitor during the dye removal process,
- characterized in that the dye redeposition inhibitor is comprised of polyesters composed according to the formula

 $X-(OCH_2-CH_2)_n-[-(OOC-R^1-COO-R^2)_u-]-OOC-R^1-COO-(CH_2-CH_2O)_n-X$ , wherein each  $\mathbf{R}^1$  residue is a 1,4-phenylene residue, optionally substituted by mono- or di- $C_1-C_3$ -alkyl; the  $\mathbf{R}^2$  residues are principally ethylene residues, 1,2-propylene residues, or mixtures thereof; each  $\mathbf{X}$  represents independently of one another hydrogen, a  $C_1$  to  $C_{12}$  hydrocarbon residue, especially ethyl or methyl; each  $\mathbf{n}$  is a number from 7 to 115, and  $\mathbf{u}$  is a number from 3 to 10.

20

30

35

- 13. A method according to any one of claims 5 to 12,
- 25 **characterized in that** the polyester or polyester blend is liquid at room temperature.
  - 14. A method according to any one of the preceding claims, characterized in that for the removal of dye abrasive stones and/or enzymes, especially at least cellulases, are put into contact with the fabric in order to achieve a stonewashed look.
  - 15. A method according to any one of the preceding claims, characterized in that the dye redeposition inhibitor is put into contact with the fabric both during the stonewashing step and the preceding desizing step.

- 16. A method according to any one of the preceding claims, characterized in that the polyetherols (C) have from 16 to 180 C<sub>2</sub> to C<sub>4</sub> alkylene oxide units.
- 17. A method according to any one of claims 1, 2, and/or 7 to 11, **characterized in that** the polyester is not made utilizing polyols having at least 3 OH groups.
- 18. The method according to claim 12, characterized in that the polyesters have molecular weights of less than 5,000 g/mole.
- 19. Use of the polyester defined by any one of claims 1 to 13 and/or 16 to 18 for preventing or minimizing dye redeposition onto textile fabrics during stonewashing or biostoning of indigo-dyed cotton fabrics.
  - 20. Indigo-dyed cotton fabric, characterized in that the indigo-dyed cotton fabric is produced in the presence of a polyester during a stonewashing or biostoning process in order to prevent dye redeposi-

tion and the polyester is defined by any one of claims 1 to 13 and/or 16 to 18.

25

20

5

30

D03008 PCPCFUI\_claims